A Pulsed Field Ionization Study of the Dissociative Photoionization Reaction $CD_4 + h\nu \rightarrow CD_3^+ + D + e^-$

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Abstract:

We have examined the energetics and dynamics of the reaction $CD_4 + h\nu \rightarrow CD_3^+ + D + e^-$ near its 0 K threshold or appearance energy (AE) using the pulsed field ionization-photoelectron (PFI-PE) and PFI-PE-photoion coincidence methods. This study yields a value of 14.4184 ± 0.0010 eV for the 0 K AE, which has allowed accurate determination of the 0 K bond dissociation energies for $D-CD_3^+$ (1.746 ± 0.003 eV) and $D-CD_3$ (4.5881 ± 0.0012 eV). The PFI-PE spectrum for CD_4 is found to exhibit a sharp step at the 0 K $AE(CD_3^+)$, indicating that the dissociation of excited CD_4 in high-n ($n\geq100$) Rydberg states at energies above the AE occurs in $\leq10^{-7}$ s. We have examined the consistency of the available energetic data for CD_3/CD_3^+ and CD_4/CD_4^+ with those for CH_3/CH_3^+ and CH_4/CH_4^+ and found that the two data sets are in excellent accord after taking into account the zero point vibrational energy corrections.

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I.   Introduction

The recent successful implementation of synchrotron-based pulsed field ionization (PFI)-photoelectron (PFI-PE)[1,2] and PFI-PE-photoion coincidence (PFI-PEPICO)[3] methods at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) has greatly enhanced the potential of PFI techniques for routine high-resolution photoionization measurements. Since the PFI-PE detection is free from the hot-electron tail problem, we have demonstrated in previous PFI-PEPICO studies[4,5] that accurate 0 K dissociative photoionization threshold or appearance energies (AEs) for a range of molecules can be determined unambiguously by the disappearance energy for the parent ion.

Due to the importance of CH_4/CH_4^+ and CH_3/CH_3^+ in combustion, atmospheric and interstellar chemistry, numerous photoionization studies have been made on CH_4, resulting in highly accurate energetic data for these species.[4] In comparison, the investigation of the deuterated species CD_4/CD_4^+ and CD_3/CD_3^+ was sparse. The only previous AE measurement for the reaction

$$CD_4 + h\nu \rightarrow CD_3^+ + D + e^- \qquad\qquad (1)$$

was made by a photoionization efficiency (PIE) study, obtaining an AE value of 14.38±0.03 eV.[6]

This Letter presents the results of a PFI-PE and PFI-PEPICO study of reaction (1) near its 0 K AE. We show that the 0 K $AE(CD_3^+)$ from CD_4 can be determined unambiguously by the disappearance energy of parent CD_4^+ with an error limit of ±0.001 eV.[4,5] Furthermore, a sharp step at the 0 K $AE(CD_3^+)$ is resolved in the PFI-PE spectrum for CD_4, indicating that excited CD_4^* fragments into $CD_3^* + D$ in a time scale $\leq 10^{-7}$ s, where CD_4^* and CD_3^* represents CD_4 and CD_3 in high-n (n≥100) Rydberg states.[7] We have also found that the available energetic data for CD_4/CD_4^+ and CD_3/CD_3^+ are consistent with those for CH_4/CH_4^+ and CH_3/CH_3^+ after taking into account the zero point vibrational energies (ZPVEs) for these molecular species.

II. Experimental

The PFI-PE and PFI-PEPICO experiments were conducted using the high-resolution VUV facility of the Chemical Dynamics Beamline with the ALS operating in the two-bunch mode.[1-3,8] In the present experiment, Ar was used in the gas filter to suppress higher undulator harmonics with photon

energies (hν) greater than 15.76 eV. In the two-bunch operation, the ALS period (656 ns) consists of two VUV bunches (bunch width = 50 ps) separated by a dark gap of 328 ns. A 2400 lines/mm grating (dispersion = 0.64 Å/mm) was used to disperse the first order undulator harmonic with entrance/exit slits set in the range of 30-100 μm. The hν calibration was achieved using the $Ar^+(^2P_{3/2})$ and $Xe^+(^2P_{3/2})$ PFI-PE bands. Previous experiments indicate that the accuracy of such a calibration is within ±0.5 meV.[8]

The PFI-PE and PFI-PEPCO measurements were achieved by employing the time-of-flight (TOF) scheme.[2,3] The PFI pulse (height =7.3 V/cm, width=180 ns) was applied ≈20 ns after the start of the dark gap. The PFI pulse also served to extract PFI-photoions toward the ion detector.[3] The average accumulation time for a PFI-PEPICO TOF spectrum is ≈20 min. Although the overall light intensity is significantly lower in this two-bunch mode operation, the larger dark gap available is more favorable for PFI-PEPICO measurements.[3] The PFI-PEPICO resolution achieved is ≈1.0 meV (FWHM).

The CD_4 sample (obtained from Aldrich, purity = 99.99%) was mixed with high purity He at a 1:10 ratio prior to expansion through a stainless steel nozzle at a stagnation pressure of 760 Torr and a stagnation temperature of 298 K. Using the same beam production system described previously,[4,5,8] the photoionization chamber maintained a pressure of $<10^{-6}$ Torr during the experiment. All PFI-PEPICO measurements were made using the supersonic CD_4/He beam sample. We estimate that CD_4 at the photoionization/photoexcitation region consists of ≈85% cold beam sample and ≈15% thermal background in the photoionization chamber. We have also recorded a PEI-PE spectrum for CD_4 using an effusive CD_4 sample for comparison with that obtained using the supersonic beam sample

III.   Results and Discussion

Selected PFI-PEPICO TOF spectra for CD_3^+ and CD_4^+ in the hν region of 14.35-14.43 eV are depicted in Fig. 1. At hν<14.40 eV, the parent CD_4^+ ion peak at 21.84 μs has the dominant intensity. As the hν is increased in the range of 14.400-14.418 eV, the intensity for the daughter CD_3^+ ion peak at 20.70 μs increases rapidly with the concomitant decrease for CD_4^+. Although the CD_3^+ peak is overwhelmingly dominant at hν≥14.4184 eV, a small CD_4^+ peak is discernible in the TOF spectrum. This small CD_4^+ signal is attributed to coincidence background caused by hot electrons dispersed into the dark gap.[9,10]

Similar to previous PFI-PEPICO studies,[3,4] the TOF peak shapes for parent CD_4^+ and daughter CD_3^+ are analyzed to consist of the contribution of a narrow component due to the cold CD_4 beam sample

and a broad component arising from the thermal CD_4 background using two Gaussian functions with widths of ≈ 100 ns and ≈ 300 ns, respectively. We note that the PFI-PEPICO TOF peaks appear to be slightly asymmetric. This is likely caused by a finite misalignment of the molecular beam and the VUV beam, such that the average flight times for ions formed by photoionization of the thermal and cold samples are slightly different.[10] The previous studies indicated that the TOF peak could be distorted due to the pulsed extraction scheme used in the PFI-PEPICO measurements.[3,4] The overall fits are indicated as solid lines in Fig. 1. The broad CD_3^+ peak observed in the TOF spectrum at $h\nu = 14.4302$ eV is caused by the kinetic energy release of reaction (1). Figure 2(a) shows the breakdown curves (i.e., fractional abundances plotted as a function of $h\nu$)[3,4] for CD_3^+ (open squares) and CD_4^+ (open circles) constructed by including the entire (cold and thermal) ion signals for CD_3^+ and CD_4^+. The breakdown curves constructed based only on the cold CD^+ and CD_4^+ ion signals are shown in Fig. 2(b). The rise and fall of the respective breakdown curves for CD_3^+ and CD_4^+ manifest finite internal rovibrational excitations of parent CD_4. Due to the rotational cooling of CD_4 achieved in the supersonic expansion, the cold breakdown curves of Fig. 2(b) are sharper, showing the complete dissociation of excited CD_4^+ to CD_3^+ + D in an energy interval of ≈ 15 meV.

We have shown previously that the 0 K AE can be determined by the disappearance energy of the parent ion in a PFI-PEPICO study.[3,4] Due to the small coincidence background for CD_4^+, the disappearance energy is manifested as the sharp break [marked by arrows in Figs. 2(a) and 2(b)] of the breakdown curves for CD_4^+. Although the shapes of the two sets of break down curves obtained by including and excluding the dissociation of thermal CD_4 are quite different, the disappearance energies for the parent CD_4^+ are identical. The disappearance energy of CD_4^+ is the energy at which even the coldest part of the CD_4 energy distribution reaches above the dissociation threshold. Thus, the disappearance energy of CD_4^+ is an intrinsic feature and can be used to provide an unambiguous determination of the 0 K AE(CD_3^+) independent of the internal energy distribution of CD_4.

We have also simulated the breakdown diagrams of Figs. 2(a) and 2(b) using procedures described previously.[9,10] The simulation assumes that the ion energy resolution is infinitely narrow and that the broadening of the breakdown diagram is due solely to the thermal excitation of parent CD_4. The thermal energy distribution in CD_4 was determined by calculating the density of rovibrational states using the Beyer-Swinehart direct count algorithm[11] based on the known vibrational frequencies and rotational

constants for CD_4. Due to the relatively high vibration frequencies for CD_4, the thermal energy for this system is mainly contributed by rotational excitations. By assuming a temperature of 40 K for cold CD_4 in the supersonic beam, we have obtained an excellent fit (solid lines) of the cold breakdown curves shown in Fig. 2(b). The dashed lines in Fig. 2(a) are simulated breakdown curves, which have taken into account the contribution of a minor component of thermal CD_4 background together with the major component of cold CD_4 in the supersonic beam.[10] The simulation also assumes a constant coincidence background for CD_4^+, which results in a constant fractional abundances of $\approx 6\%$ and $\approx 3\%$ for CD_4^+ in Figs. 2(a) and 2(b), respectively.[10] This simulation is consistent with the conclusion that the break at 14.4184 ± 0.0010 eV resolved in the breakdown curves of Figs. 2(a) and 2(b) is a distinct feature, which can be taken as the 0 K $AE(CD_3^+)$. Figure 3 shows a magnified view of the simulated and experimental breakdown data for CD_4^+, together with their error bars, in the region of 14.410-14.447 eV. The designations of symbols used in Figs 2(a), 2(b), and 3 are identical. It is clear in Fig. 3 that the break marking the 0 K $AE(CD_3^+)$ at 14.4184eV can be determined unambiguously to within ± 0.0010 eV by the breakdown curve for CD_4^+ shown in either Fig. 2(a) or Fig. 2(b).

In previous studies, we have identified sharp step-like features in the PFI-PE spectra for CH_4 and C_2H_2, marking precisely the corresponding 0 K AEs for CH_3^+ and C_2H^+ determined in PFI-PEPICO measurements.[3,4,7] A detailed discussion concerning the conditions for the observation of a step at the 0 K AE of a dissociative photoionization process has been given.[7] Figure 2(c) compares the PFI-PE spectra for CD_4 in the region of 14.30-14.50 eV obtained using an effusive sample (upper spectrum, solid circles) and a supersonic beam sample (lower spectrum, open circles). Although the PFI-PE spectrum obtained using an effusive CD_4 sample shows a general increase in PFI-PE intensity as the hν is increased, a step at the 0 K $AE(CD_3^+)$ is not discernible. The PFI-PE spectrum for CD_4 obtained using the cold beam sample clearly reveals a sharp step [marked as 0 K AE in Fig. 2(c)]. The observation of this step can be attributed to the lifetime switching effect[7] at the 0 K $AE(CD_3^+)$, where CD_4^* species with shorter lifetimes are converted into CD_3^* fragments with longer lifetimes. The longer lifetime observed for CD_3^* results from the fact that CD_3^* formed at the AE has an energy below the $IE(CD_3)$ and thus cannot decay via autoionization. The observation of the sharp step in the PFI-PE spectrum indicates[7] that the conversion from CD_4^* to CD_3^* at energy above the AE of reaction (1) is complete prior to PFI and that process (1)

has a dissociation rate constant $\geq 10^7$ s^{-1}. This step resolved in the PFI-PE spectrum for CD_4 can be taken as a confirmation for the 0 K $AE(CD_3^+)$=14.4184±0.0010 eV determined in the PFI-PEPICO study.

The dissociation leading to the production of CD_3^* from CD_4^* formed by VUV excitation of thermally excited CD_4 occurs below the 0 K AE. As a result of the magnification of PFI events for CD_3^* fragments, the PFI-PE spectrum observed using an effusive beam of CD_4 [upper spectrum in Fig. 2(c)] is expected to manifest a higher nominal temperature than the actual temperature of the effusive sample. This would result in the efficient filling of the step in the PFI-PE spectrum. Thus, the step associated with the 0 K AE cannot be readily identified in the PFI-PE spectrum using a thermal sample.

The 0 K $AE(CD_3^+)$ =14.4184±0.0010 eV determined here is significantly more precise compared to the previous PIE value of 14.38 ± 0.03 eV.[6] These values along with selected literature IE values[12-17] for CD_3 and CD_4 are listed in Table I. The $IE(CD_4)$=12.672±0.003 eV[12] and $IE(CD_3)$=9.8303±0.0006 eV[15] determined in recent PFI studies are likely the most accurate among previous measurements. Based on these IE values and the 0 K $AE(CD_3^+)$ determined here, we have calculated the 0 K bond dissociation energies as $D_0(D-CD_3^+) = AE(CD_3^+)–IE(CD_4) = 1.746±0.003$ eV and $D_0(D-CD_3) = AE(CD_3^+)-IE(CD_3) = 4.5881±0.0012$ eV. The experimental 0 K or 298 K heats of formation ($\Delta_f H°_0$ or $\Delta_f H°_{298}$) for CD_3 and CD_4 are not available. Krishna et al.[18] has calculated the $\Delta_f H°_0$ and $\Delta_f H°_{298}$ values for CD_3 and CD_4 by statistical methods using the known $\Delta_f H°_0$ and $\Delta_f H°_{298}$ values for CH_3 and CH_4. The conversion requires the ZPVEs for CH_4, CD_4, CH_3, and CD_3 (see Table II),[18] which are calculated using known experimental vibrational frequencies of these species. The D_0 values for CD_4 and CD_4^+ and the statistically derived $\Delta_f H°_0$ and $\Delta_f H°_{298}$ values for CD_3 and CD_4 are also listed in Table I.

Using the $\Delta_f H°_0(D)$=52.535±0.001 kcal/mol,[19] together with the 0 K $AE(CD_3^+)$ (332.50±0.02 kcal/mol) and $\Delta_f H°_0(CD_4)$ (-19.214±0.1 kcal/mol),[18] we obtain $\Delta_f H°_0(CD_3^+) = 260.75±0.10$ kcal/mol based on process (1). If we combine the $IE(CD_3)$=9.8303±0.0006 eV[15] and $\Delta_f H°_0(CD_3)$ (33.90±0.10 kcal/mol),[18] we derive the value $\Delta_f H°_0(CD_3^+)$ =260.59±0.10 kcal. The excellent agreement of the latter value with that of 260.75±0.10 kcal/mol derived using process (1) indicates that the experimental 0 K $AE(CD_3^+)$, $IE(CD_3)$, and derived $\Delta_f H°_0(CD_3)$ and $\Delta_f H°_0(CD_4)$ values are highly reliable. Combining the $IE(CD_4^+)$ (292.22±0.07 kcal/mol) and $\Delta_f H°_0(CD_4)$ gives $\Delta_f H°_0(CD_4^+) = 273.01±0.12$ kcal/mol. The latter value along with the $\Delta_f H°_0(CD_3^+)$ value derived using process (1) is included in Table I.

Since not all the vibrational frequencies for CH_4^+, CD_4^+, CH_3^+, and CD_3^+ are known, accurate experimental ZPVEs for these cations cannot be obtained. We have calculated the ZPVEs at the MP2(Full)/6-311++G(3d2f,2pd) level of theory.[20] Comparing the experimental and theoretical ZPVEs for the neutral species,[18] we obtain an average scaling factor of 0.957 for the theoretical ZPVEs. The scaled theoretical ZPVEs are given in Table II. Using these scaled theoretical ZPVEs, we have calculated values (given in parentheses in Table II) for the $IE(CD_3)$, $IE(CD_4)$, $D_0(D\text{-}CD_3)$, $D_0(D\text{-}CD_3^+)$, and $AE(CD_3^+)$ based on corresponding values for $IE(CH_3)$,[21] $IE(CH_4)$, $D_0(H\text{-}CH_3)$, $D_0(H\text{-}CH_3^+)$, and $AE(CH_3^+)$.[12,20] Since the error bars assigned to these calculated values have ignored the uncertainties associated with the theoretical ZPVEs, they represent lower limits. As shown in Table II, the calculated (values in parentheses) and experimental (values in bold fonts) are in good agreement, indicating that the available experimental IE, D_0, AE, values for CH_4/CH_4^+, CH_3/CH_3^+, CD_4/CD_4^+ and CD_3/CD_3^+ are reliable. The small discrepancies between the calculated and experimental IE, D_0, and AE values for CD_4/CD_4^+ and CD_3/CD_3^+ can be attributed to errors of the theoretical ZPVEs used.

The highly accurate energetic data (values in bold fonts in Tables I and II) would provide a challenge for state-of-the-art *ab initio* computational quantum theories. Currently, the Gaussian2/Gaussian-3 (G2/G3) procedures[22,23] are among the most popular quantum chemical computation schemes. The G2/G3 theories are slightly semi-empirical in nature because they contain a high level correction obtained empirically from a fit to a set of experimental energetic data by minimizing the deviations between corresponding experimental results and predicted values. The accuracy of such a fitting scheme is limited by the accuracy of experimental data used. We have compiled the G2/G3 values for $AE(CD_3^+)$, $IE(CD_4)$, $IE(CD_3)$, and $\Delta H^\circ_{f0}/\Delta H^\circ_{f298}$ of CD_3, CD_3^+, CD_4, and CD_4^+ for comparison with the best experimental values in Table I.[22,23] As expected, the G3 predictions show a consistently better agreement with the best experimental values than the G2 results. The G2/G3 predictions are generally in agreement with the experimental values, achieving the target accuracy[22,23] of ≈ 1 kcal/mol for the computational procedures. We note that the precisions of the best experimental values listed in Tables I and II are significantly better than that can be achieved by G2/G3 calculations. Accurate AE, IE, and ΔH°_{f0} values, such as those listed in Tables I and II with error limits in the meV range, should play an important role in the development of the next generation of *ab initio* quantum computational procedures.

IV.   Conclusions

We have examined the dissociation reaction of energy-selected CD_4^+ to form $CD_3^+ + D$ near its threshold using PFI techniques. The 0 K $AE(CD_3^+)$ obtained has made possible the determination of accurate $D_0(D\text{-}CD_3^+)$, $D_0(D\text{-}CD_3)$, and $\Delta H°_{f0}(CD_3^+)$ values through appropriate thermochemical cycles. The sharp step-like feature appearing at the 0 K $AE(CD_3^+)$ observed in the PFI-PE spectrum of CD_4 is consistent with the lifetime switching effect,[7] indicating that the dissociation of reaction (1) at energies above its threshold occurs in a time scale of $\leq 10^{-7}$ s. We found that the energetic data for CH_4/CH_4^+ and CH_3/CH_3^+ are in excellent accord with those for CD_4/CD_4^+ and CD_3/CD_3^+ after taking into accounts the ZPVEs of these species.

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Table I. Comparison of ΔH°_{f0} values for CD_3, CD_3^+, CD_4, and CD_4^+, 0 K $AE(CD_3^+)$ from CD_4, and D_0 values for CD_3-D and CD_3^+-D.[a]

$AE(CD_3^+)$ (eV)	IE (eV)		ΔH°_{f0} (kcal/mol)[e]				D_0(eV)[b]	
	CD_4	CD_3	$CD_4{}^f$	$CD_4{}^{+g}$	$CD_3{}^f$	$CD_3{}^{+h}$	CD_3-D	CD_3^+-D
14.4184±0.0010[b]	**12.672±0.003[c]**	**9.8303± 0.0006[d]**	**-19.21±0.10** (-21.09±0.10)	**273.01±0.12** (271.50±0.12)	**33.90±0.10[f]** (33.14±0.10)	**260.75±0.10** (259.93±0.10)	**4.5881 ±0.0012**	**1.746 ±0.003**
14.38±0.03[i]	12.658 ± 0.015[j]	9.832±0.002[k]						
	12.882 ± 0.008[l]	9.831 ± 0.007[m]						
Semi-empirical G3/G2 values[n]								
14.41/14.39	12.70/12.73	9.86/9.77	-19.8/-20.2 (-21.6/-22.1)	273.2/273.4 (271.6/271.8)	32.7/33.8 (32.2/33.3)	260.0/259.1 (259.1/258.3)	4.55/4.62	1.71/1.66

a)   The values in bold fonts are the best experimental values.
b)   This work
c)   Reference 12
d)   Reference 15
e)   The values in parentheses are ΔH°_{f298} values. The ΔH°_{f298} values for CD_3 and CD_4 are from Ref. 18 and those for CD_3^+ and CD_4^+ are converted from the corresponding ΔH°_{f0} values in the present study.
f)   Reference 18
g).   References. 12 and 18
h)   This work and Ref. 18. Calculated using reaction (1)
i)   Reference 6
j)   Reference 16
k)   Reference 13
l)   Reference 17
m)   Reference 14
n)   References 22 and 23

Table II. Zero point vibrational energies (ZPVEs), IE, D_0, and AE values for CH_4/CH_4^+, CH_3/CH_3^+, CD_4/CD_4^+, and CD_3/CD_3^+.[a]

X	ZPVE (eV)[b]				IE (eV)		D_0 (eV)		AE (eV)
	CX_4	CX_3	CX_4^+	CX_3^+	CX_4	CX_3	CX_3^+-X	CX_3-X	CX_3^+
H	1.183 **1.1755[c]**	0.790 **0.7896[c]**	1.014	0.832	**12.618±0.004[d]**	**9.8380±0.0004[e]**	**1.705±0.004[g]**	**4.485±0.001[g]**	**14.323±0.001[g]**
D	0.868 **0.8683[c]**	0.580 **0.5850[c]**	0.744	0.615	**12.672±0.003[d]** (12.664±0.004)[i]	**9.8303±0.0006[f]** (9.8291±0.0004)[i]	**1.746±0.003[h]** (1.754±0.004)[i]	**4.5881±0.0012[h]** (4.591±0.001)[i]	**14.4184±0.0010[h]** (14.421±0.001)[i]

a) The values in bold fonts represent the best experimental values. The values in parentheses are converted from corresponding IE or D_0 or AE values of CH_n or CH_n^+ (n=3, 4) using the scaled theoretical ZPVEs (see the text).
b) The upper values are scaled (scaling factor=0.957) ZPVEs calculated at the MP2(Full)/6-311++G(3d2f,2pd) level of theory.
c) Calculated using the experimental vibrational frequencies given in Ref. 18
d) Reference 12
e) Reference 20
f) Reference 15
g) Reference 4
h) This work
i) The error limits have not taken into account the errors for the scaled ZPVEs and are thus lower bounds.

Figure Captions

Figure 1   Selected PFI-PEPICO TOF spectra for CD_3^+ and CD_4^+ in the hν range of 14.3578-14.4302 eV. The respective TOF peaks for CD_3^+ and CD_4^+ are centered at 20.69 and 21.87 μs. The solid lines are simulated spectra (see the text).

Figure 2   Breakdown curves of CD_3^+ and CD_4^+ in the hν range of 14.30-14.47 eV. (a) The experimental fractional abundances for CD_3^+ and CD_4^+ obtained based on the entire ion signal are shown as (O) and (□), respectively. The dashed lines (− −) are the simulated curves. (b) The experimental fractional abundances for CD_3^+ and CD_4^+ obtained based only on the cold ion signals are indicated as (●) and (■), respectively. The continuous lines (──) are the simulated curves obtained by assuming a sample temperature of 40 K. (c) PFI-PE spectra obtained using an effusive sample (solid circles, upper spectrum) and a supersonic molecular beam sample (open circles, lower spectrum). The step at the 0 K AE is discernible in the lower PFI-PE spectrum.

Figure 3   A magnified view of the breakdown curve for CD_4^+ based on the entire ion signals (O) and that based only on the cold ion signals (●) in the hν range of 14.410-14.447 eV. Both curves show a sharp break at 14.4184±0.0010 eV, which is taken to be the 0 K $AE(CD_3^+)$.